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Exodentate versus Endodentate Coordination of a Crown Thioether Ligand in Silver(I) Complexes of 2,5,8-Trithia[9]-*o*-benzenophane (TT[9]OB). Structures of [Ag(TT[9]OB)$_2$][X] (X = ClO$_4$, BPh$_4$, CF$_3$SO$_3$)

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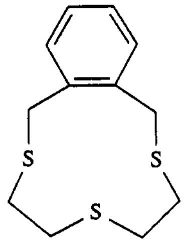
The crown thioether ligand 2,5,8-trithia[9]-*o*-benzenophane, TT[9]OB, is known to have an exodentate conformation in the uncomplexed form; the sulfur donor atoms are oriented away from the center of the macrocyclic ring. This ligand reacts with AgX (X = ClO_4^-, BF_4^-, BPh_4^-, $CF_3SO_3^-$) in a 2:1, ligand to metal ratio to give complexes of the general formula [Ag(TT[9]OB)$_2$][X]. Although these complexes are simple mononuclear species, the solid-state structures vary dramatically with the counterion X. The complex [Ag(TT[9]OB)$_2$][ClO$_4$] crystallized in the space group $P2_1/n$ with a = 8.317 (2) Å, b = 26.178 (11) Å, c = 13.361 (5) Å, β = 101.14 (2)°, V = 2854 (3) Å^3, and Z = 4. The structure refined to R = 7.06% and R_w = 7.58% for 1577 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Ag atom is in an octahedral environment defined by the six S atoms of two facially coordinated TT[9]OB ligands. The complex [Ag(TT[9]OB)$_2$][BF$_4$] is isostructural with [Ag(TT[9]OB)$_2$][ClO$_4$]. The complex [Ag(TT[9]OB)$_2$][BPh$_4$] crystallized in the space group $C2/c$ with a = 16.257 (5) Å, b = 16.031 (6) Å, c = 16.962 (4) Å, β = 93.25 (3)°, V = 4413 (4) Å^3, and Z = 4. The structure refined to R = 6.79% and R_w = 6.90% for 1495 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Ag atom is in a distorted tetrahedral coordination environment defined by two S atoms from each TT[9]OB ligand. The complex [Ag(TT[9]OB)$_2$][CF$_3$SO$_3$] crystallized in the space group $P\bar{1}$ with a = 12.390 (2) Å, b = 14.158 (4) Å, c = 9.290 (3) Å, α = 91.04 (3)°, β = 109.64 (2)°, γ = 83.37 (2)°, V = 1524.9 (9) Å^3, and Z = 2. The structure refined to R = 6.76% and R_w = 7.28% for 2815 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Ag atom is in a tetrahedral coordination environment defined by three S atoms from one facially coordinated TT[9]OB ligand and one S atom from the other TT[9]OB ligand which has an exodentate conformation. Variable-temperature ^{1}H NMR spectroscopy indicates that a rapid fluxional process interconverts the observed geometries in solution and that the most favorable solution structure is a symmetric one. Solution oxidation potentials are consistent with an octahedral S$_6$ environment at Ag(I).

Introduction

The coordination chemistry of 1,4,7-trithiacyclononane (9S3)[1-4] and the molecular structures of cyclic and acyclic polythioethers[5] suggest that if SCH$_2$CH$_2$S linkages are to be used as the structural basis of metal-binding ligands, some perturbation should exist which forces S donor atoms to be preorganized in an endodentate conformation. The incorporation of rigid xylyl units into crown thioethers may limit the conformational flexibility of the macrocycle ring or introduce conformational strain into the macrocycle backbone, resulting in an endodentate conformation or disposition toward such a conformation.

The coordination chemistry of 2,5,8-trithia[9]-*o*-benzenophane (TT[9]OB) is unique with respect to these conformational requirements. Although the conformation of the free ligand is exodentate,[6] there is considerable strain involved in the SCH$_2$CH$_2$SCH$_2$CH$_2$S bracket and the ligand easily converts to an endodentate conformation, as evidenced by the isolation and structural characterization of the complexes [Mo(CO)$_3$(TT[9]OB)],[6] [Cu(Ph$_2$PMe)(TT[9]OB)][ClO$_4$],[7] [Ag(PPh$_3$)(TT[9]OB)][ClO$_4$],[7] [PdCl$_2$(TT[9]OB)],[8] and [Rh(COD)(TT[9]OB)][BF$_4$],[9] in which TT[9]OB assumes an endodentate conformation and is coordinated facially as a tridentate ligand. Herein, we report the synthesis and structures of a series of complexes of general formula [Ag(TT[9]OB)$_2$][X] (X = ClO_4^-, BF_4^-, BPh_4^-, $CF_3SO_3^-$), in which the solid-state structures vary with the type of noncoordinating counterion.[10] The variety of conformations for TT[9]OB observed in the solid state and the solution behavior of the [Ag(TT[9]OB)$_2$]$^+$ cations demonstrate that the metal-promoted interconversion of these ligand conformations is a low-energy process for this macrocyclic thioether ligand.



TT[9]OB

Experimental Section

TT[9]OB[6,7] and AgBPh$_4$[11] were prepared by the literature methods. AgClO$_4$, AgBF$_4$, AgCF$_3$SO$_3$, all organic reagents, and all solvents were purchased from Aldrich and used as received. All reactions were conducted under an atmosphere of N$_2$ using standard Schlenk techniques, and all solvents were degassed prior to use. ^{1}H NMR spectra were recorded at 300.1 MHz on a Bruker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analysis were performed by Microanalytical Services, New Westminister, British Columbia, Canada. Cyclic voltammetric experiments were performed using a BAS CV-27 potentiostat with a platinum-disk working electrode, a Ag/AgCl reference electrode, and [NBu$_4$][PF$_6$] as the supporting electrolyte. All potentials are quoted versus ferrocene/ferrocenium, Fc/Fc$^+$.

Preparation of [Ag(TT[9]OB)$_2$][X] (X = ClO_4^-, BF_4^-, BPh_4^-, $CF_3SO_3^-$). To a solution of TT[9]OB (0.100 g, 0.390 mmol) in CH$_3$CN (10 mL) was added AgX (0.195 mmol). The resulting colorless solution was stirred at room temperature for 3 h. The solvent was removed under vacuum and the crude white product recrystallized from CH$_3$CN. X = ClO_4^-: yield 135 mg (96%). Anal. Calcd for C$_{24}$H$_{32}$AgClO$_4$S$_6$: C, 40.02; H, 4.49; S, 26.71. Found: C, 39.98; H, 4.33; S, 26.44. X = BF_4^-: yield 90 mg (90%). Anal. Calcd for C$_{24}$H$_{32}$AgBF$_4$S$_6$: C, 40.73; H, 4.57; S, 27.19. Found: C, 40.12; H, 4.44; S, 26.56. X = $CF_3SO_3^-$: yield 144 mg (96%). Anal. Calcd for C$_{25}$H$_{32}$AgF$_3$O$_3$S$_7$: C, 39.00; H, 4.20; S, 29.16. Found: C, 38.88; H, 4.10; S, 28.93. X = BPh_4^-: yield 150 mg (91%). Anal. Calcd for C$_{48}$H$_{52}$AgBS$_6$: C, 61.32; H, 5.59; S, 20.47. Found: C, 60.87; H, 5.32; S, 20.38. ^{1}H NMR (300 K, CD$_3$CN, cation resonces only): δ 7.28–7.41 (m, 4 H, aromatic), 3.90 (s, 4 H, benzylic), 2.83–2.93 ppm (m, 8 H, SCH$_2$CH$_2$SCH$_2$CH$_2$S).

General X-ray Diffraction Data Collection, Solution, and Refinement. Diffraction experiments were performed on a four-circle Rigaku AFC6S diffractometer with graphite-monochromatized Mo Kα radiation. Cell constants and orientation matrices for data collection were obtained from least-squares refinements using the setting angles of 25 centered reflections. Machine parameters, crystal data, and data collection parameters

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Table I. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for $[Ag(TT[9]OB)_2][ClO_4]$, $[Ag(TT[9]OB)_2][BPh_4]$, and $[Ag(TT[9]OB)_2][CF_3SO_3]$

chem formula	$C_{24}H_{32}AgClO_4S_6$	$C_{48}H_{52}AgBS_6$	$C_{25}H_{32}AgF_3O_3S_7$
fw	720.28	940.08	769.93
a, Å	8.317 (2)	16.257 (5)	12.390 (2)
b, Å	26.178 (11)	16.031 (6)	14.158 (4)
c, Å	13.361 (5)	16.962 (5)	9.290 (3)
α, deg			91.04 (3)
β, deg	101.14 (2)	93.25 (3)	109.64 (2)
γ, deg			83.37 (2)
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
V, Å^3	2854 (3)	4413 (4)	1524.5 (9)
ρ(calcd), g/cm^{-3}	1.676	1.270	1.657
Z	4	4	2
μ, cm^{-1}	12.45 (empirical)	6.17 (empirical)	11.59 (empirical)
λ, Å	0.71069	0.71069	0.71069
T, °C	24	24	24
$R(F_o)$,[a] %	7.06	6.79	6.76
$R_w(F_o)$,[a] %	7.58	6.90	7.28

[a] $R = \sum||F_o| - |F_c|/\sum|F_o||$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$, and $w = 1/\sigma^2(F)$.

are summarized in Table I. The intensities of three standard reflections were recorded periodically and showed no statistically significant changes over the duration of the data collections. An empirical absorption correction, based on Ψ-scan data, was applied to each data set. The data sets were processed by using the TEXSAN software package running on a VAX 3520 workstation.[12] Refinements were carried out by using full-matrix least-squares techniques on *F* minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[13] and anomalous dispersion terms[14,15] were taken from the usual sources. Fixed H atom contributions were included with C–H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameter of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued.

Structure Determination of $[Ag(TT[9]OB)_2][ClO_4]$. Colorless crystals of $[Ag(TT[9]OB)_2][ClO_4]$ were grown by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. A statistical analysis of intensity distributions and a determination of systematic absences were consistent with the space group $P2_1/n$, and this was confirmed by a successful solution refinement. A total of 5139 reflections were collected, and 1577 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The position of the silver atom was determined by the conventional heavy-atom method, and the remaining non-hydrogen atoms were located from difference Fourier map calculations. In the final cycles of refinement, the silver, sulfur, chlorine, and oxygen atoms were assigned anisotropic thermal parameters and the carbon atoms were assigned isotropic thermal parameters. This resulted in $R = \sum||F_o| - |F_c|/\sum|F_o|| = 0.0706$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0758$ at final convergence. A goodness of fit calculation resulted in a value of 1.74. The Δ/σ value for any parameter in the final cycle was less than 0.01, and a final difference Fourier map calculation showed no peaks of chemical significance. Selected atomic positional parameters are summarized in Table II, and selected bond distances and angles are summarized in Table III. Positional parameters (Table S-II), nonessential bond distances and angles (Table S-III), thermal parameters (Table S-IV), hydrogen atom parameters (Table S-V), and values of $10|F_o|$ and $10|F_c|$ (Table S-XIV) are deposited as supplementary material.

Table II. Selected Positional Parameters and *B*(eq) for $[Ag(TT[9]OB)_2][ClO_4]$

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ag	0.7522 (2)	0.37439 (8)	0.24848 (13)	4.76 (7)
S1	1.0336 (6)	0.3637 (2)	0.1682 (4)	4.1 (3)
S2	0.6780 (7)	0.2925 (2)	0.1187 (4)	4.1 (3)
S3	0.5698 (6)	0.4214 (2)	0.0827 (4)	3.2 (2)
S4	0.9270 (6)	0.3166 (2)	0.4084 (5)	4.1 (3)
S5	0.8702 (6)	0.4479 (2)	0.3862 (4)	4.0 (3)
S6	0.4799 (6)	0.3924 (2)	0.3261 (4)	3.5 (2)
C1	0.842 (2)	0.4795 (7)	0.088 (1)	3.3 (4)
C2	0.795 (2)	0.5224 (7)	0.128 (1)	3.8 (4)
C3	0.898 (3)	0.5531 (9)	0.198 (2)	5.3 (5)
C4	1.060 (2)	0.5385 (7)	0.222 (2)	4.2 (5)
C5	1.110 (2)	0.4932 (8)	0.185 (1)	4.1 (4)
C6	1.006 (2)	0.4649 (7)	0.117 (2)	3.6 (4)
C7	1.064 (2)	0.4156 (8)	0.082 (2)	4.5 (5)
C8	0.999 (2)	0.3072 (8)	0.086 (2)	5.4 (5)
C9	0.885 (2)	0.2701 (8)	0.112 (2)	5.2 (5)
C10	0.617 (2)	0.3249 (7)	0.003 (1)	4.0 (4)
C11	0.494 (2)	0.3668 (7)	0.047 (13)	3.8 (4)
C12	0.717 (2)	0.4500 (7)	0.015 (2)	3.9 (4)
C13	0.489 (2)	0.2918 (7)	0.3789 (13)	2.3 (4)
C14	0.349 (2)	0.2717 (8)	0.320 (2)	4.3 (4)
C15	0.362 (2)	0.2268 (8)	0.277 (2)	4.4 (5)
C16	0.498 (3)	0.1985 (9)	0.288 (2)	5.6 (5)
C17	0.643 (2)	0.2177 (8)	0.350 (2)	4.5 (5)
C18	0.636 (2)	0.2659 (7)	0.3997 (14)	2.8 (4)
C19	0.783 (2)	0.2840 (8)	0.472 (2)	4.7 (5)
C20	1.009 (3)	0.3640 (9)	0.506 (2)	5.9 (5)
C21	1.033 (3)	0.4152 (9)	0.466 (2)	6.6 (6)
C22	0.709 (3)	0.4509 (9)	0.458 (2)	5.5 (5)
C23	0.542 (2)	0.4504 (8)	0.399 (2)	4.7 (5)
C24	0.472 (2)	0.3434 (8)	0.424 (2)	4.6 (5)

Table III. Selected Bond Distances and Angles for $[Ag(TT[9]OB)_2][ClO_4]$

	Distances (Å)		
Ag–S1	2.771 (6)	S4–C20	1.84 (2)
Ag–S2	2.752 (6)	S5–C21	1.77 (2)
Ag–S3	2.725 (5)	S5–C22	1.79 (2)
Ag–S4	2.788 (6)	S6–C23	1.83 (2)
Ag–S5	2.712 (6)	S6–C24	1.84 (2)
Ag–S6	2.709 (5)	C1–C12	1.50 (2)
S1–C7	1.83 (2)	C6–C7	1.48 (3)
S1–C8	1.83 (1)	C8–C9	1.45 (3)
S2–C9	1.84 (2)	C10–C11	1.51 (2)
S2–C10	1.82 (2)	C13–C24	1.50 (2)
S3–C11	1.81 (2)	C18–C19	1.48 (2)
S3–C12	1.82 (2)	C20–C21	1.47 (2)
S4–C19	1.81 (2)	C22–C23	1.46 (3)
	Angles (deg)		
S1–Ag–S2	77.3 (2)	C11–S3–C12	103.3 (9)
S1–Ag–S3	96.3 (2)	C19–S4–C20	100.0 (10)
S1–Ag–S4	83.6 (2)	C21–S5–C22	105.5 (11)
S2–Ag–S5	96.4 (2)	C23–S6–C24	104.1 (10)
S2–Ag–S6	175.8 (2)	S1–C7–C6	111 (1)
S2–Ag–S3	79.5 (2)	S1–C8–C9	115 (2)
S2–Ag–S4	94.6 (2)	S2–C9–C8	118 (2)
S2–Ag–S5	171.2 (2)	S2–C10–C11	111 (1)
S2–Ag–S6	105.9 (2)	S3–C11–C10	117 (1)
S3–Ag–S4	173.9 (2)	S3–C12–C1	110 (1)
S3–Ag–S5	107.7 (2)	S4–C19–C18	112 (1)
S3–Ag–S6	81.8 (2)	S4–C20–C21	114 (2)
S4–Ag–S5	78.3 (2)	S5–C21–C20	121 (2)
S4–Ag–S6	98.7 (2)	S5–C22–C23	116 (2)
S5–Ag–S6	80.6 (2)	S6–C23–C22	116 (2)
C7–S1–C8	104.3 (10)	S6–C24–C13	109 (1)
C9–S2–C10	102.2 (10)		

Structure Determination of $[Ag(TT[9]OB)_2][BPh_4]$. Colorless crystals of $[Ag(TT[9]OB)_2][BPh_4]$ were grown by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. A statistical analysis of intensity distributions and a determination of systematic absences were consistent with the space group $C2/c$, and this was confirmed by a successful solution refinement. A total of 4058 reflections were collected, and 1495 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The position of the silver atom was determined by the conventional heavy-atom method, and the remaining non-hydrogen atoms were located from difference Fourier map calculations. In the final cycles of refinement, the silver, sulfur, boron, and carbon atoms of TT[9]OB were assigned anisotropic thermal parameters and the carbon atoms of the BPh_4^- anion were input as rigid phenyl groups and assigned isotropic thermal parameters. The central sulfur atom, S2, of TT[9]OB displayed 2-fold disorder and was successfully modeled with site occupancy factors of 72 and 28%. This resulted in $R = 0.0679$ and $R_w = 0.0690$ at final convergence. A goodness of fit calculation resulted in a value of 1.86.

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Table IV. Selected Positional Parameters and *B*(eq) for [Ag(TT[9]OB)$_2$][BPh$_4$]

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ag	0.0000	0.3153 (1)	0.2500	5.9 (1)
S1	0.1076 (2)	0.4337 (2)	0.2113 (2)	4.2 (2)
S2	0.1492 (3)	0.2230 (3)	0.1732 (3)	5.1 (2)
S3	−0.0576 (2)	0.2610 (2)	0.1169 (2)	3.9 (2)
C1	−0.0613 (7)	0.4264 (8)	0.0770 (6)	3.5 (6)
C2	−0.145 (1)	0.4407 (9)	0.0725 (7)	5.1 (8)
C3	−0.1773 (8)	0.517 (1)	0.0927 (8)	6.0 (9)
C4	−0.124 (1)	0.5787 (9)	0.1178 (7)	5.8 (8)
C5	−0.0404 (9)	0.5666 (8)	0.1246 (7)	4.3 (7)
C6	−0.0078 (8)	0.4899 (8)	0.1038 (6)	3.5 (6)
C7	0.0829 (7)	0.4759 (8)	0.1139 (6)	4.3 (7)
C8	0.2090 (7)	0.3853 (8)	0.2045 (8)	5.2 (7)
C9	0.212 (1)	0.309 (1)	0.155 (1)	9 (1)
C10	0.094 (1)	0.189 (1)	0.091 (1)	9 (1)
C11	0.0050 (9)	0.1768 (8)	0.0850 (7)	5.2 (7)
C12	−0.0326 (8)	0.3435 (7)	0.0486 (6)	4.5 (7)

Table V. Selected Bond Distances and Angles for [Ag(TT[9]OB)$_2$][BPh$_4$]

	Distances (Å)		
Ag–S1	2.688 (4)	S3–C11	1.79 (1)
Ag–S3	2.548 (3)	S3–C12	1.82 (1)
S1–C7	1.81 (1)	C1–C12	1.50 (2)
S1–C8	1.83 (1)	C6–C7	1.49 (2)
S2–C9	1.76 (2)	C8–C9	1.49 (2)
S2–C10	1.70 (2)	C10–C11	1.46 (2)
	Nonbonded Distances (Å)		
Ag···S2	3.183 (5)	Ag···S2A	3.94 (2)
	Angles (deg)		
S1–Ag–S3	103.7 (1)	S1–C7–C6	109.1 (8)
S1–Ag–S1′	90.1 (2)	S1–C8–C9	116.5 (9)
S1–Ag–S3′	104.3 (1)	S2–C9–C8	120.0 (12)
S3–Ag–S3′	140.0 (2)	S2–C10–C11	125.5 (13)
C7–S1–C8	104.8 (6)	S3–C11–C10	117.1 (10)
C9–S2–C10	113.2 (9)	S3–C12–C1	110.9 (8)
C11–S3–C12	101.8 (6)		

The Δ/σ value for any parameter in the final cycle was less than 0.01, and a final difference Fourier map calculation showed no peaks of chemical significance. Selected atomic positional parameters are summarized in Table IV, and selected bond distances and angles are summarized in Table V. Positional parameters (Table S-VI), nonessential bond distances and angles (Table S-VII), thermal parameters (Table S-VIII), hydrogen atom parameters (Table S-IX), and values of $10|F_o|$ and $10|F_c|$ (Table S-XV) are deposited as supplementary material.

Structure Determination of [Ag(TT[9]OB)$_2$][CF$_3$SO$_3$]. Colorless crystals of [Ag(TT[9]OB)$_2$][CF$_3$SO$_3$] were grown by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. A statistical analysis of intensity distributions was consistent with the space group $P\bar{1}$, and this was confirmed by a successful solution refinement. A total of 5622 reflections were collected, and 2815 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The positions of the silver atom and four of the seven sulfur atoms were determined by direct methods from the *E* map with highest figure of merit. The remaining non-hydrogen atoms were located from a difference Fourier map calculation. In the final cycles of refinement, the silver, sulfur, and carbon atoms of the cation were assigned anisotropic thermal parameters and the anion was input as rigid CF$_3$ and SO$_3$ groups, each with 2-fold disorder and overall isotropic group thermal parameters. This resulted in $R = 0.0676$ and $R_w = 0.0728$ at final convergence. A goodness of fit calculation resulted in a value of 2.02. The Δ/σ value for any parameter in the final cycle was less than 0.04, and a final difference Fourier map calculation showed no peaks of chemical significance. Selected atomic positional parameters are summarized in Table VI, and selected bond distances and angles are summarized in Table VII. Positional parameters (Table S-X), nonessential bond distances and angles (Table S-XI), thermal parameters (Table S-XII), hydrogen atom parameters (Table S-XIII), and values of $10|F_o|$ and $10|F_c|$ (Table S-XVI) are deposited as supplementary material.

Table VI. Selected Positional Parameters and *B*(eq) for [Ag(TT[9]OB)$_2$][CF$_3$SO$_3$]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Ag	0.56321 (8)	0.17496 (7)	0.5476 (1)	4.04 (5)
S1	0.7075 (3)	0.0944 (2)	0.4240 (4)	4.7 (2)
S2	0.4095 (3)	0.0967 (2)	0.3295 (4)	4.9 (2)
S3	0.4717 (3)	0.3314 (2)	0.3994 (4)	4.5 (2)
S4	0.6517 (2)	0.1429 (2)	0.8260 (3)	3.7 (1)
S5	0.6616 (3)	0.4484 (3)	0.9449 (5)	6.2 (2)
S6	1.0274 (3)	0.3446 (3)	1.1429 (5)	6.9 (2)
C1	0.691 (1)	0.355 (1)	0.415 (1)	4.7 (7)
C2	0.736 (2)	0.431 (1)	0.515 (2)	7 (1)
C3	0.851 (2)	0.419 (2)	0.619 (2)	9 (1)
C4	0.918 (2)	0.340 (2)	0.618 (3)	9 (1)
C5	0.879 (1)	0.272 (1)	0.524 (2)	6.4 (9)
C6	0.766 (1)	0.275 (1)	0.421 (1)	4.4 (6)
C7	0.733 (1)	0.192 (1)	0.321 (1)	5.7 (7)
C8	0.611 (1)	0.031 (1)	0.274 (2)	6.5 (8)
C9	0.492 (1)	0.076 (1)	0.198 (2)	6.9 (9)
C10	0.313 (1)	0.203 (1)	0.254 (2)	8 (1)
C11	0.358 (1)	0.293 (1)	0.236 (2)	8 (1)
C12	0.571 (1)	0.367 (1)	0.308 (2)	7.0 (8)
C13	0.962 (1)	0.1578 (8)	1.093 (1)	3.7 (6)
C14	1.027 (1)	0.133 (1)	1.244 (1)	4.5 (6)
C15	1.014 (1)	0.051 (1)	1.311 (1)	4.7 (6)
C16	0.936 (1)	−0.007 (8)	1.232 (2)	4.8 (7)
C17	0.866 (1)	0.0175 (9)	1.082 (7)	4.2 (6)
C18	0.880 (1)	0.0996 (9)	1.013 (1)	3.7 (6)
C19	0.805 (1)	0.1179 (6)	0.845 (1)	4.3 (6)
C20	0.650 (1)	0.2547 (9)	0.923 (1)	4.1 (6)
C21	0.646 (1)	0.342 (1)	0.830 (1)	5.0 (6)
C22	0.821 (1)	0.448 (1)	1.003 (2)	7.1 (9)
C23	0.886 (1)	0.393 (1)	1.150 (2)	6.2 (8)
C24	0.987 (1)	0.245 (1)	1.023 (25)	5.5 (7)

Table VII. Selected Bond Distances and Angles for [Ag(TT[9]OB)$_2$][CF$_3$SO$_3$]

	Distances (Å)		
Ag–S1	2.600 (4)	S5–C21	1.81 (1)
Ag–S2	2.590 (3)	S5–C22	1.86 (2)
Ag–S3	2.570 (3)	S6–C23	1.83 (2)
Ag–S4	2.476 (3)	S6–C24	1.79 (1)
S1–C7	1.81 (2)	C1–C12	1.48 (2)
S1–C8	1.80 (1)	C6–C7	1.49 (2)
S2–C9	1.84 (2)	C8–C9	1.49 (2)
S2–C10	1.81 (2)	C10–C11	1.47 (2)
S3–C11	1.82 (2)	C13–C24	1.51 (2)
S3–C12	1.83 (2)	C18–C19	1.54 (2)
S4–C19	1.84 (1)	C20–C21	1.51 (2)
S4–C20	1.81 (1)	C22–C23	1.51 (2)
	Nonbonded Distances (Å)		
Ag···S5	5.251 (4)	Ag···S6	7.115 (5)
	Angles (deg)		
S1–Ag–S2	84.6 (1)	S1–C7–C6	112 (1)
S1–Ag–S3	107.3 (1)	S1–C8–C9	118 (1)
S1–Ag–S4	106.0 (1)	S2–C9–C8	113 (1)
S2–Ag–S3	85.2 (1)	S2–C10–C11	121 (1)
S2–Ag–S4	133.8 (1)	S3–C11–C10	117 (1)
S3–Ag–S4	130.4 (1)	S3–C12–C1	110 (1)
C7–S1–C8	102.7 (7)	S4–C19–C18	111 (1)
C9–S2–C10	104.3 (8)	S4–C20–C21	116 (1)
C11–S3–C12	101.2 (8)	S5–C21–C20	120 (1)
C19–S4–C20	102.1 (6)	S5–C22–C23	114 (1)
C21–S5–C22	98.6 (7)	S6–C23–C22	109 (1)
C23–S6–C24	99.8 (6)	S6–C24–C13	118 (1)

Results

Synthesis and Solution Studies. Silver(I) complexes of the formula [Ag(TT[9]OB)$_2$][X], where X is one of the noncoordinating anions ClO$_4^-$, BF$_4^-$, BPh$_4^-$, or CF$_3$SO$_3^-$, were prepared by reacting 2 equiv of TT[9]OB with 1 equiv of AgX in CH$_3$CN at room temperature. The resulting colorless solids can be isolated in >90% yield and recrystallized by vapor diffusion of diethyl ether into a CH$_3$CN solution of the complex. The crystalline materials are air stable, and only the BPh$_4^-$ complex shows sensitivity to light.

The ^{1}H NMR spectra of these complexes exhibit characteristics of a highly fluxional system. At 300 K in CD$_3$CN, the only solvent in which all four complexes have comparable solubilities, averaged

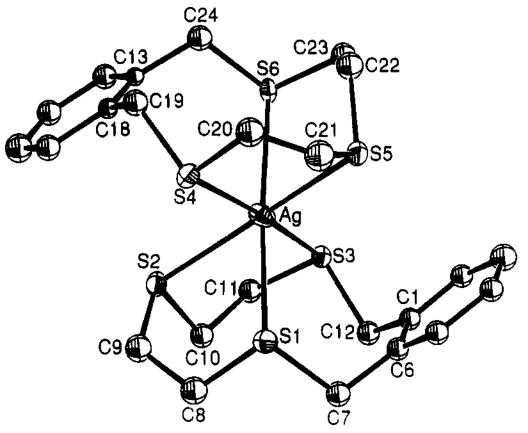

Figure 1. Perspective ORTEP drawing of the $[Ag(TT[9]OB)_2]^+$ cation for $[X] = ClO_4^-$, showing the atom-numbering scheme.

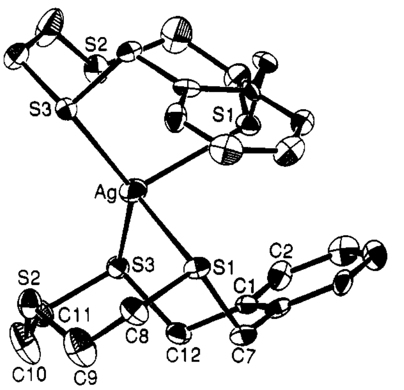

Figure 2. Perspective ORTEP drawing of the $[Ag(TT[9]OB)_2]^+$ cation for $[X] = BPh_4^-$, showing the atom-numbering scheme.

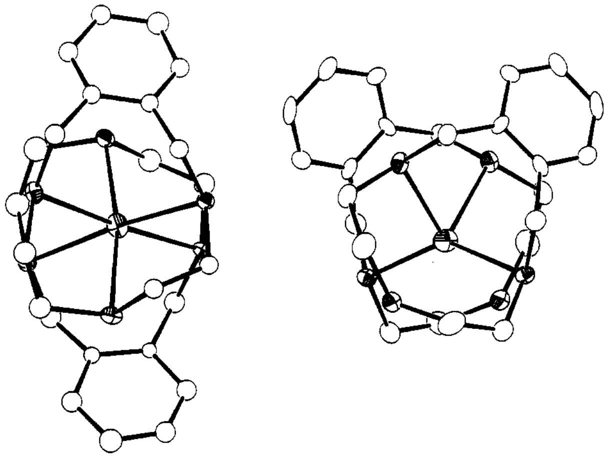

Figure 3. Perspective ORTEP drawings of the $[Ag(TT[9]OB)_2]^+$ cations for $[X] = ClO_4^-$ and BPh_4^-, showing the relative orientations of the ligands.

signals are observed for aromatic (δ 7.28–7.41 ppm (m, 4 H)), benzylic (δ 3.90 ppm (s, 4 H)), and SCH_2CH_2S (δ 2.83–2.93 (m, 8 H)) protons. When the sample is cooled to 235 K in CD_3CN, only broadening and loss of resolution occurs for these resonances; however, the use of $(CD_3)_2CO$ as a solvent for complexes with $X = CF_3SO_3^-$ and BPh_4^- allowed recording of lower temperature ^1H NMR spectra for these two complexes, and some further resolution was evident. At 170 K, the aromatic region remains completely unresolved, δ 7.41 (4 H), but the benzylic protons are split into a broad doublet of doublets, δ 4.12 (4 H), and the methylenic protons of the SCH_2CH_2S chain are separated into a large, broad multiplet, δ 3.69 (4 H), and a broad doublet, δ 3.24 (4 H). The gross features of these spectra are very similar to the well-resolved, limiting spectra found for complexes such as $[Cu(TT[9]OB)(PPh_3)][ClO_4]$, in which TT[9]OB is symmetrically coordinated in an endodentate conformation.[7]

The possibility of oxidation of the Ag(I) cation to a Ag(II) species, which has been observed for $[Ag(9S3)_2]^+$, $[Ag(18S6)]^+$, and $[Ag(16S6)]^+$ was investigated.[16–19] Cyclic voltammetry of $[Ag(TT[9]OB)_2]^+$ in CH_3CN (0.1 M $[NBu_4][PF_6]$) at platinum electrodes showed an oxidation at $E_{pa} = 0.70$ V versus Fc/Fc$^+$ which is essentially irreversible; only a small return wave was observed, indicating that the oxidized product is unstable in CH_3CN at 298 K. This is similar to the results observed for $[Ag(9S3)_2]^+$, $[Ag(18S6)]^+$, and $[Ag(16S6)]^+$. The S_6 homoleptic coordination spheres found in these crown thioether complexes result in relatively low oxidation potentials, $E_{pa} = 0.79$, 1.00, and 0.87, respectively, and are attributed to a higher electron density at the metal center, which promotes oxidation.

X-ray Structure of $[Ag(TT[9]OB)_2][ClO_4]$. The unit cell contains four $[Ag(TT[9]OB)_2]^+$ cations and four $[ClO_4]^-$ anions. A perspective view of the $[Ag(TT[9]OB)_2]^+$ cation for this complex is shown in Figure 1. Selected bond distances and angles are found in Tables III and S-III.

The Ag atom is in an S_6 thioether environment with approximately octahedral geometry. Both the TT[9]OB ligands are in endodentate conformations, and these two tridentate ligands sandwich the metal ion. Figure 3 shows that the relative orientation of the TT[9]OB ligands is such that the cation has a molecular center of symmetry, although this is not imposed crystallographically. The Ag–S distances are 2.771 (6), 2.725 (5), 2.712 (6), and 2.709 (5) Å for S1, S3, S4, and S6 attached to the xylyl fragment and 2.752 (6) and 2.788 (6) Å for the central S2 and S4 atoms. The S–Ag–S angles for the five-membered chelate rings are 77.3 (2), 79.5 (2), 78.3 92), and 80.6 (2)°, and the S–Ag–S angles for the seven-membered chelate rings involving the *o*-xylyl fragment are 96.3 (2) and 98.7 (2)°. The S–C and C–C bond distances are all within expected limits. The ClO_4^- anion has expected tetrahedral geometry, and the Cl–O bond distances and O–Cl–O angles are normal.

X-ray Structure of $[Ag(TT[9]OB)_2][BPh_4]$. The unit cell contains four $[Ag(TT[9]OB)_2]^+$ cations and four $[BPh_4]^-$ anions, each of which has crystallographic 2-fold site symmetry. A perspective view of the $[Ag(TT[9]OB)_2]^+$ cation for this complex is shown in Figure 2. Selected bond distances and angles are found in Tables V and S-VII.

The Ag atom is in a severely distorted tetrahedral coordination sphere defined by two S atoms from each TT[9]OB ligand with the central S atom of each ligand oriented away from the metal center. Figure 3 shows the relative orientation of the TT[9]OB ligands and emphasizes the crystallographic 2-fold axis relating the halves of the cation. The Ag–S distances are 2.688 (4) and 2.548 (2) Å for S1 and S3 and 3.183 (5) and 3.94 (5) Å for the two sites of the disordered, nonbonded central S2 atom. The S1–Ag–S3 angle for the seven-membered chelate ring is 103.7 (1)°, and the interligand angles are 90.1 (2), 104.3 (1), and 140.0 (2)° for S1–Ag–S1′, S1–Ag–S3′, and S3–Ag–S3′. The S–C and C–C bond distances are all within expected limits. The BPh_4^- anion has expected tetrahedral geometry, and the B–C bond distances and C–B–C angles are normal.

X-ray Structure of $[Ag(TT[9]OB)_2][CF_3SO_3]$. The unit cell contains two $[Ag(TT[9]OB)_2]^+$ cations and two $[CF_3SO_3]^-$ anions. A perspective view of the $[Ag(TT[9]OB)_2]^+$ cation for this complex is shown in Figure 4. Selected bond distances and angles are found in Tables VII and S-XI.

The Ag atom is in a tetrahedral geometry with three coordination sites occupied by facial coordination to the S atoms of one TT[9]OB ligand with an endodentate conformation and the fourth

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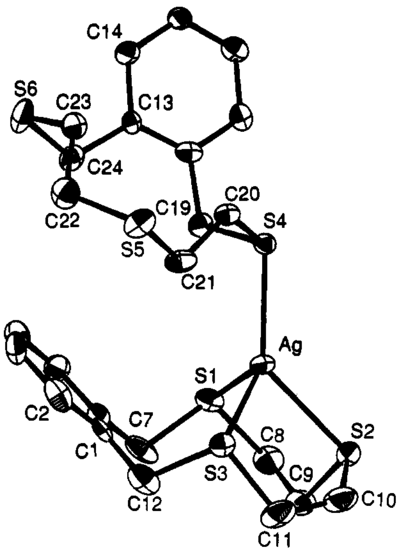

Figure 4. Perspective ORTEP drawing of the $[Ag(TT[9]OB)_2]^+$ cation for [X] = $CF_3SO_3^-$, showing the atom-numbering scheme.

site occupied by the S atom of another TT[9]OB ligand with an exodentate conformation. The Ag–S distances to the endodentate ligand are 2.600 (4), 2.590 (3), and 2.570 (3) Å for S1, S2, and S3 are 2.476 (2) Å to the S4 atom of the exodentate ligand. The S–Ag–S angles for the five-membered chelate rings are 84.6 (1) and 85.2 (1)°, and the S–Ag–S angle for the seven-membered chelate ring is 107.3 (1)°. The S–Ag–S angles between the exodentate and endodentate ligands are 106.0 (1), 133.8 (1), and 130.4 (1)° to S1, S2, and S3, respectively. The S–C and C–C bond distances are all within expected limits. The only refined distance in the $CF_3SO_3^-$ anion was the S–C distance, which was disordered over two sites with distances of 1.74 (2) and 1.75 (2) Å.

Discussion

The previously determined X-ray structure of TT[9]OB shows that this molecule is essentially an *o*-xylyl fragment fused to a $SCH_2CH_2SCH_2CH_2S$ chain such that the ligand adopts an exodentate conformation with the sulfur donors oriented away from the center of the macrocyclic cavity.[6] An interesting structural feature of TT[9]OB is that the $SCH_2CH_2SCH_2CH_2S$ linkage shows S–C–C–S torsional angles averaging 162 (4)° compared to 180° for the ideal "bracket" conformation usually observed in thioethers.[4,5] The effect of this distortion is to introduce strain into the $SCH_2CH_2SCH_2CH_2S$ unit, thereby lowering the overall energy difference between the exodentate and endodentate conformations. Molecular mechanics calculations have shown that the energy difference between exodentate and endodentate conformations of TT[9]OB is significantly less than that between analogous conformations for the isomeric 2,5,8-trithia[9]-*m*-benzenophane, TT[9]MB, for which there is no distortion of the $SCH_2CH_2SCH_2CH_2S$ linkage.[6] Therefore, although the introduction of an *o*-xylyl fragment did not result in preorganization of the S donor sites, it did perturb the conformation in favor of an exodentate to endodentate transformation.

Silver(I) is ideal for investigating the coordination chemistry of thioether ligands, such as TT[9]OB. The metal shows a strong affinity for thioether donors, and Ag(I) has very weak stereochemical demands, often yielding complex geometries dictated by the conformational preferences of the ligand rather than the bonding demands of the metal ion.[7,18] Since there appear to be relatively small energy differences between the possible ligand conformations for TT[9]OB, it might be expected that the solution structure of $[Ag(TT[9]OB)]^+$ would be fluxional due to metal-promoted interconversions between conformations. This is exactly what is observed. The room-temperature ^1H NMR spectra of these complexes are consistent with a highly fluxional system independent of the anion used, and low-temperature spectra are consistent with a symmetrical coordination mode. Since electrochemical measurements show an oxidation potential similar to those of other complexes with an S_6 coordination sphere, octahedral geometry is assumed to be favored for the $[Ag(TT[9]OB)_2]^+$ cation in solution.

Table VIII. Comparison of Torsional Angles for TT[9]OB in the Complexes $[Ag(TT[9]OB)_2][X]$[a]

	torsional angles, deg			
sequence	ClO_4^-	BPh_4^-	$CF_3SO_3^-$ (endo)	$CF_3SO_3^-$ (exo)
C1–C6–C7–S1	−87 (2)	−86.9 (11)	−104 (1)	−115 (1)
C6–C7–S1–C8	149 (1)	160.4 (8)	155 (1)	65.5 (9)
C7–S1–C8–C9	−145 (2)	−68.8 (12)	−70 (1)	81.5 (9)
S1–C8–C9–S2	56 (2)	−56 (2)	−62 (2)	−173.0 (6)
C8–C9–S2–C10	51 (2)	128.6 (13)	148 (1)	92 (1)
C9–S2–C10–C11	−152 (1)	−126.8 (14)	−59 (2)	−90 (1)
S2–C10–C11–S3	68 (2)	49 (2)	−49 (2)	150.6 (8)
C10–C11–S3–C12	65 (1)	62.8 (12)	135 (1)	−79 (1)
C11–S3–C12–C1	−154 (1)	−165.5 (8)	−151 (1)	−76 (1)
S3–C12–C1–C6	111 (2)	111.4 (11)	95 (2)	146 (1)
C12–C1–C6–C7	−5 (3)	−6 (2)	−1 (2)	−1 (2)

[a] Sign is positive for a clockwise rotation of 1 to 4 viewed down the 2–3 bond. Values for BPh_4^- include only the major (78%) disorder model.

The unexpected result from this study is that the solid-state structures observed for the $[Ag(TT[9]OB)_2]^+$ cations are dependent upon the noncoordinating anions. Since there are no significant cation–anion interactions in the solid state, the effect of X^- on the structure of $[Ag(TT[9]OB)_2]^+$ must be the crystal-packing compatibility of $[Ag(TT[9]OB)_2]^+$ and X^-. It appears that each differently shaped and sized anion prefers to crystallize with a different structural form of $[Ag(TT[9]OB)_2]^+$. If it is assumed that there is a rapid interchange of these cationic structures in solution, it may be that the crystallized species is simply the least soluble one due to a favorable cation–anion match.

For the "spherical" anions X = ClO_4^- and BF_4^-, both TT[9]OB ligands are in an endodentate conformation, resulting in a pseudooctahedral geometry. The same coordination geometry occurs for $[Ag(9S3)_2]^+$ and is attributed to the preorganized, endodentate conformation of 9S3.[18] However, the ability to enforce facial coordination at a metal center appears to be possible with TT[9]OB, in spite of the lack of preorganization. For the larger spherical anion X = BPh_4^-, both TT[9]OB ligands adopt an unusual conformation in which the S atoms adjacent to the xylyl ring are endodentate and coordinated to the metal center, while the two central S atoms are exodentate. Figure 3 shows the relative orientations of the two ligands in this distorted tetrahedral complex and demonstrates the difference between the coordination geometries of the cations for X = ClO_4^- and BF_4^- and for X = BPh_4^-. The relationship between these two structures can be thought of as a 90° rotation about the vector along which the drawings in Figure 3 are projected. This would occur with a concomitant breaking of the Ag–S2 bonds and a conformational change to make S2 exodentate. This is similar to the rhombic or Ray–Dutt twist used to describe racemization in octahedral, tris chelate complexes.[20] The interconversion of octahedral complexes through this type of distorted tetrahedral intermediate may represent a feasible pathway for the fluxionality observed in solution.

The structure of the $[Ag(TT[9]OB)_2]^+$ cation in the complex in which the counterion is $CF_3SO_3^-$ is the most significant of the series. $[Ag(TT[9]OB)_2][CF_3SO_3]$ is the first example of a crown thioether complex in which both the exodentate and endodentate conformations of a macrocycle are bonded to the same metal ion. The conformation observed for the terminally bound, exodentate ligand is essentially that found in the X-ray structure of the free ligand.[6] The corresponding structural parameters for the endodentate ligand compare very closely to those found for the pseudotetrahedral complex $[Ag(PPh_3)(TT[9]OB)][ClO_4]$ in which

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PPh_3 occupies the fourth coordination site rather than an exodentate TT[9]OB molecule.[7] Table VIII lists the torsional angles in TT[9]OB for these different $[Ag(TT[9]OB)_2]^+$ cations. Although there are some differences in the chelate ring conformations (δ versus λ), three basic ligand conformations can be distinguished for TT[9]OB: S_3 exo or exodentate, as observed in the free ligand; S_3 endo or endodentate, as found for facial coordination; and S_2 endo/S exo, the conformation which results in bidentate coordination.

Summary and Conclusions

Solution behavior and solid-state structures of the complexes $[Ag(TT[9]OB)_2][X]$ demonstrate that TT[9]OB is capable of easily converting from an exodentate to an endodentate conformation. This property can be attributed to the strain introduced into the free ligand as a result of the incorporation of a rigid *o*-xylyl group. This results in a number of significant observations. (1) Similar to 9S3, TT[9]OB is capable of enforcing octahedral coordination at Ag(I) by sandwiching the ion between two capping ligands. This occurs even though the sulfur donors are not preorganized as in 9S3. (2) TT[9]OB can adopt three different coordination modes and act as a two-, four-, or six-electron donor ligand bonding through one, two, or three sulfur atoms. This combination of apparently strong metal–ligand interaction and conformational flexibility makes TT[9]OB unique in crown thioether chemistry.

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Supplementary Material Available: Listings of crystallographic data collection parameters, positional parameters, thermal parameters, nonessential bond distances and angles, and hydrogen atom parameters (Table S-I–S-XIII) (12 pages); listings of observed and calculated structure factors (Table S-XIV–S-XVI) (22 pages). Ordering information is given on any current masthead page.

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Halogenated Derivatives of the Dimolybdenum Tetraphosphoxane Cage

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Iodination and chlorination of the dimolybdenum tetraphosphoxane cage complex $(CO)_4Mo[{}^iPr_2NPO]_4Mo(CO)_4$ in dichloromethane afforded first the mixed-valent products $X_2(CO)_2Mo[{}^iPr_2NPO]_4Mo(CO)_4$ and then the tetrahalo complexes $X_2(CO)_2Mo[{}^iPr_2NPO]_4Mo(CO)_2X_2$ (X = Cl, I). The tetrabromo complex can be similarly synthesized, but the dibromo complex is not formed by stoichiometric bromination in CH_2Cl_2. It was indirectly prepared by metathesis from the diiodo product in $CH_2Cl_2/CH_3C{\equiv}N$. The integrity of the adamantane-like $Mo_2P_4O_4$ cage is maintained in all these halogenation products. For the cage–I_2 complex, an intermediate species, $I_2(CO)_3Mo[{}^iPr_2NPO]_4Mo(CO)_4$, can be observed at low temperature. This readily decarbonylates to give the isolated product. A single-crystal X-ray structural determination of the diiodo complex, $I_2(CO)_2Mo[{}^iPr_2NPO]_4Mo(CO)_4$, has been completed. Crystal data: monoclinic, $P2_1/c$, $a = 18.915$ (2) Å, $b = 11.911$ (2) Å, $c = 21.063$ (2) Å, $\beta = 94.88$ (1)°, $V = 4728.4$ (9) Å^3, $Z = 4$, $D_{calc} = 1.610$ g/cm^3, $\mu = 19.8$ cm^{-1}, $F(000) = 1919.51$, Mo Kα ($\lambda = 0.70930$ Å), $R_F = 0.058$, and $R_w = 0.049$ for 4029 unique observed $[|F| \geq 2.5\sigma(F)]$ reflections and 468 parameters. A trigonal-prismatic coordination sphere is found around the 16-electron Mo(II) center. NMR spectroscopic data support the retention of this geometry for all the dihalogenated and tetrahalogenated species in solutions of nonpolar solvents. By contrast to these stable products, halogenation of the phenyl-substituted cage complex, $(CO)_4Mo[PhPO]_4Mo(CO)_4$, afforded $X_2(CO)_3Mo[PhPO]_4Mo(CO)_4$ and $X_2(CO)_3Mo[PhPO]_4Mo(CO)_3X_2$. These complexes show low stability, lose CO readily, and are only poorly characterized.

Introduction

One of the most fundamental reaction types of group VI transition-metal diphosphine carbonyl complexes is that with elemental halogens.[1] Typically halogen oxidation of the zerovalent metal to 2+ is accompanied by coordination of two halides as well as loss of one or more carbon monoxide ligands. This is sometimes called an oxidative-elimination reaction. Often, stereochemically nonrigid seven-coordinate complexes of the type $M(CO)_3(PR_3)_2X_2$ are isolated.[2] Structural work on these have revealed capped octahedral as well as pentagonal-bipyramidal geometries for these 18-electron species. Depending on the phosphine ligands and halides, reversible CO loss to generate six-coordinate $M(CO)_2(PR_3)_2X_2$ complexes can also occur.[3] These and related Mo(II) and W(II) complexes without phosphine ligands are formally electron deficient with only 16 metal valence electrons, and substantial structural departures from the preeminent octahedral stereochemistry can be expected due to a first-order Jahn–Teller effect.[4] This is especially prevalent in the presence of π-donating ligands. Thus the molecular structure of $Mo(CO)_2[S_2CN{}^iPr_2]_2$ is trigonal prismatic, while $Mo(O\text{-}{}^tBu)_2(CO)_2Py_2$ has a bicapped tetrahedral coordination sphere.[5] Halides can also be expected to function as π donors in the 16-electron $M(CO)_2(PR_3)_2X_2$ family of complexes. Indeed, $Mo(PPh_3)_2(CO)_2Br_2$ has been shown to distort toward a bicapped tetrahedral geometry.[6] By contrast, chelating diphosphines have so far yielded exclusively electron-precise seven-coordinate $Mo(CO)_3$(diphosphine)X_2 products.[7] We have been investigating the halogenation reactions of the dimolybdenum octacarbonyl *cyclo*-tetraphosphoxane complexes $(CO)_4Mo[{}^iPr_2NPO]_4Mo(CO)_4$ (**1**) and $(CO)_4Mo[PhPO]_4Mo(CO)_4$ (**2**), both of which feature two $Mo(CO)_4$(diphosphine) centers constrained in an adamantanoid cage structure.[8] We are interested in the resulting stereochemistry at the Mo(II) centers,

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(1) Early examples include: (a) Cook, C. D.; Nyholm, R. S.; Tobe, M. L. *J. Chem. Soc.* **1965**, 4194. (b) Lewis, J.; Whyman, R. *J. Chem. Soc.* **1965**, 5486. (c) Colton, R.; Rix, C. J. *Aust. J. Chem.* **1969**, *22*, 305.

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